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INTERACTION BETWEEN CLAYS AND ORGANIC COMPOUNDS IN SOILS. PART 1. MECHANISMS OF INTERACTION BETWEEN CLAYS AND DEFINED ORGANIC COMPOUNDS

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1. Introduction

In a recent review in this Journal (Jacks, 1963) it was stated that "the union of mineral and organic matter to form the organo-mineral complex [is] a synthesis as vital to the continuance of life as, and less understood than, photosynthesis." Part of the reason that it is less understood than photosynthesis is that its importance has not been so widely recognised. There are other reasons. The interaction between clays and organic materials in soils is a difficult field to investigate. Not only are there many uncertainties still remaining regarding the constitution of the bulk of the organic material that is present, but the precise condition of the surfaces with which union takes place is seldom known. These surfaces may be the relatively simple ones indicated by the known structures of clay minerals, but they may also be surfaces of amorphous or poorly crystallized oxides or hydroxides of silicon, aluminium and iron, present as such or as encrustations on the surfaces of clay minerals. Even for clay minerals with "clean" surfaces much remains to be learnt of the distribution of charges at the surface. Finally the interaction between inorganic and organic materials occurs in a multicomponent system which is a further complication of the phenomenon.

There have recently been advances in the understanding of the adsorption of simple and polymeric organic compounds and in the knowledge of the chemical composition and physicochemical properties of the organic compounds in soils that throw some light on the mechanism of interaction. These advances enable a better appreciation of the rather diverse information concerning the interactions of clays and organic compounds in soils, and the properties of the clay-organic complex, to be obtained.

2. Proportion of Soil Organic Matter Contained in the Clay-Organic Complex

The proportion of organic matter involved in the clay-organic complex is not very readily determined. An extremely wide range of bonding mechanisms can occur from simple mechanical entanglement to the formation of multiple chemical bonds. To separate the "free" and "combined" organic material some amount of work must be applied, and the proportion of material found in the complex will depend on the magnitude of this work. However the somewhat limited data available indicate that free and entangled material is separable from bonded material, even when the bonding is due to relatively weak, physical adsorption forces. The most satisfactory method of achieving the separation is by flotation of the free organic material in a liquid of density intermediate to that of the free material and clay-organic complex (Lein, 1940; Henin and Turc, 1950; Henin, Monnier and Turc, 1959; Khan, 1959; Monnier, Turc and Jeanson-Luusinang, 1962; Greenland and Ford, 1964). Liquids of density between 1.8 and 2.0 have been found satisfactory. Short ultrasonic dispersion (Greenland and Ford, 1964) is probably the best method of releasing entangled material, but entanglement can also be largely overcome by boiling an aqueous suspension of the soil and then washing and drying from alcohol to prevent reaggregation (Monnier, Turc and Jeanson-Luusinang, 1962).

Results obtained by various workers are collected in Table 1. It can be seen that except in extremely sandy soils a very considerable proportion of the organic material is associated with the inorganic components. Henin and Turc (1950), Khan (1959) and Greenland and Ford (1964) have all presented evidence that the free material is in a much earlier stage of decomposition than the combined material. Greenland and Ford (1964) determined the U.V. light absorption at 260 mμ of that part of the free material brought into solution by 0.5 N caustic soda, and compared it with the absorption at the corresponding wavelength of the humic acids obtained by treating the whole soil with alkali. The light fraction contained very little material absorbing at this wavelength so that the humic acids in the soils examined must have been mostly present in the clay-organic complex.

The separation of free organic material leaves a residue containing both the clay-organic complex and some "free" inorganic material. By sedimentation in liquids of density 2.2-2.5 further separations can be achieved (Henin and Turc, 1950; Khan, 1959). The data available indicate that most of the clay-sized material is associated with the clay-

organic complex, and the "free" inorganic material is predominantly sand and silt. It is possible that [illegible] actions also have surface coatings of [illegible] ials, but as they have a very low surface area the change in the mean density is negligible.

Other methods for separating the organo-mineral complex have been suggested, but all involve chemical dispersion treatments. Even the mildest of these cause some separation of organic material from inorganic. Thus the first step in the method proposed by Tyulin (1938) involves shaking in sodium chloride. This releases organic colloids bonded to inorganic materials, probably through Ca^{++} bridge linkages, as Brydon and Sowden (1959) have stated. Subsequent treatments with dilute alkali release some iron and aluminium-bonded material, but will also dissolve some organic compounds from the "free" organic material. Thus Tyulin's method and similar ones based on a fractionation of the colloidal complex give no satisfactory information on the total amount of organic material contained in the complex, although they give some useful information which will be discussed below on the mechanism of formation of the complex.

Elutriation and sieving methods for the separation of free organic materials have been described (e.g. Roulet *et al*, 1963) but these techniques extract significantly less organic material than the density methods, although they have the advantage that they can be more readily adapted to handle large quantities of soil.

3. Adsorption of Defined Organic Compounds by Clay Minerals

General

The bonding forces which may be involved in the formation of the clay-organic complex are listed with examples in Table 2. De Boer (1953) has rightly emphasised that the forces involved in adsorption are the same as those acting in all other instances where atoms and molecules are in proximity. But when a large organic molecule approaches the surface of a clay mineral the situation is particularly complex because apart from major interactions between specific groups on the organic molecule and sites on the clay surface, minor interactions may become important because a large number of such interactions between different parts of the surface and molecule are possible. These small interactions will usually be of the same order of magnitude as the hydration forces so that competition with water molecules for the surface is important.

The total free-energy change is composed of the heat of adsorption and entropy change, a net increase in entropy favouring the adsorption reaction. Entropy is a measure of the randomness of the system, and where adsorption of one large molecule leads to the desorption of many small ones there will be a large overall entropy increase.

This displacement of water molecules from the surface of a clay may dominate the adsorption reaction (cf. Koral, Ullman and Eirich, 1958). The gain due to release of water molecules will be offset to a greater or less extent by the loss of entropy due to the restriction in freedom of the adsorbed molecule. This is dependent on the shape and configuration of the organic molecule. The extent to which the adsorbed molecule can collapse to the clay surface also determines the number of contacts made with the surface, and hence the total magnitude of the segment-surface interaction energies and the amount of previously adsorbed water which is displaced.

The various properties of adsorbent and adsorbate and of the medium in which they are dispersed which affect the adsorption process are listed in Table 3. The relative importance of these can best be appreciated by considering the various studies of the adsorption of defined organic compounds by clays and oxides. Their significance in the adsorption of soil organic compounds can then be assessed.

Adsorption by montmorillonite

(i) X-ray diffraction studies.

The importance of clay-organic interactions in industrial practices and the possibility of producing materials with completely new or extensively modified properties have attracted considerable attention to this field (see for instance the review by Nahin, 1961). Much of this work has been concerned exclusively with the clay mineral montmorillonite. For adsorption studies montmorillonite has three great advantages over other clay minerals and most other adsorbents: (i) the specific surface area (of the fully dispersed clay) is determined by its crystal structure and can be calculated without reference to adsorption data, (ii) this area is large (700-800 m^2/g), (iii) the organization of the adsorbed compound can be studied by X-ray diffraction methods.

Interlamellar adsorption of organic compounds by montmorillonite can be observed by X-ray diffraction methods very easily, and it has been shown that a very wide range of organic compounds can be adsorbed (cf. Bradley, 1945; MacEwan, 1948; Greene-Kelly, 1955a, and the reviews by Grim, 1953; MacEwan, 1950 and 1962; Calvet, 1963 and Weiss, 1961b, 1963). The X-ray observations establish the fact of adsorption, and provide information regarding the orientation of the adsorbed molecule or the number of adsorbed layers, but do not of themselves provide direct evidence relating to the mechanism of adsorption. The orientation of the adsorbed molecules is derived from correlations between the known molecular dimensions of the adsorbed molecules and the determined interlamellar separation.

It is very desirable that accurate Fourier analyses of organic complexes of montmorillonite and vermiculite should be carried out, so that the precise location of the atoms of the organic compounds can be determined with respect to the clay. Some attempts at such analyses have been made (e.g. Bradley, 1945; Brown, 1950; Franzen, 1955; Greene-Kelly, 1955a, Bradley, Weiss and Rowland, 1961) but as yet the degree of resolution achieved

is not sufficient to locate the atoms very precisely. Formidable difficulties are involved in obtaining a crystal of sufficient regularity for more detailed analysis, and in carrying out the Fourier analysis successfully. Without such analyses, however, the interpretation of the X-ray data must involve some degree of speculation. In many instances the separation is so small that only one layer of molecules lying as flat as possible can be intercalated. In other instances the orientation is less certain, but when a molecule containing a long alkyl chain of length about 30A gives rise to complexes with spacings of say 14A, 18A and another of about 40A it is reasonable to assume that the first two refer to complexes in which the molecule is lying flat on the surface and the other to a complex where the adsorbed molecule is standing in a plane perpendicular to the surface (cf. the data for such compounds discussed by Barshad, 1952 and Greenland and Quirk, 1960). However even in instances such as these the possibility of multiple layers in the interlamellar region arises (McAtee, 1958) although no conclusive evidence has been presented that such multilayer complexes are formed. Weiss (1958b) considers that in many complexes of long-chain alkylammonium ions the alkyl chains lie in a plane making a small angle with the clay surface.

Although most authors agree that the alkyl chains lie in a plane at right angles to the surface, somewhat different basal spacings have been reported. These have been interpreted in terms of different angles between the chain and the surface (cf. Franzen, 1955; Sutherland and MacEwan, 1961; Weiss, 1958b, 1963). Weiss who has studied this subject extensively considers that the angle is dependent on the surface density of charge on the clay, and Weiss and Kantner (1960) have suggested that the basal spacing of the complex formed with dodecylammonium chloride may be used to determine the surface density of charge of mica-type expanding lattice clays. The cetyl pyridinium ion is particularly strongly adsorbed so that for all clays except a few with exceptionally low densities of charge, the cetyl chains project at right angles to the surface. The pyridinium groups pack as tightly as possible to form a complete surface coverage. Thus the adsorption of cetyl pyridinium bromide can be used to determine the specific surface areas of clays (Greenland and Quirk, 1960, 1962, 1964).

In those complexes in which a single layer of organic molecules separates the adjacent alumino-silicate lamellae the distance of separation is usually slightly less than the minimum dimension of the adsorbed molecules (Brindley and Hoffmann, 1962). This has been ascribed to the formation of C-H . . .O hydrogen bonds between the methylene groups and the oxygens of the clay surface (Bradley, 1945; MacEwan, 1948; Talibudeen, 1955; Greenland, 1956a), to keying of the molecules into the clay surface (Glaeser, 1951; Barrer and Perry, 1961; Rowland and Weiss, 1961; Greenland, Laby and Quirk, 1962) or to general attractions between the surface and the adsorbed molecules (Greene-Kelly, 1955a). The first of these involves a specific adsorption mechanism, and if correct would represent an important general contribution to the adsorption of organic compounds by clays. Unfortunately there is no unequivocal evidence that C-H . . .O bonds are formed. Although the interlamellar separation may be as much as 1.2A less than the minimum dimension of the adsorbed molecules, this can be accounted for by uncertainties in the van der Waals radii of the atoms involved and the possibility that the adsorbed molecules may penetrate the hexagonal "holes" in the clay surface. Furthermore it has been shown (Radoslovich, 1960) that surfaces of mica crystals are not flat, but that the oxygen tetrahedra may be tilted, and this introduces a further uncertainty. However the most conclusive evidence that C-H . . .O bonds do not normally contribute to the adsorption of organic compounds is provided by the infrared spectra of the complexes. This is discussed below.

(ii) Adsorption isotherms.

X-ray diffraction studies of themselves provide only limited information about the adsorption of organic compounds by expanding-lattice clays, but they contribute a valuable adjunct to studies by other methods. Determination and interpretation of the adsorption isotherm, and spectroscopic examination of the complexes, are the most useful of these. Since interaction in the soil takes place in the presence of water only adsorption from aqueous solution is relevant here. Giles *et al*, (1960) have presented a detailed analysis and classification of isotherms for adsorption from solution. This has greatly simplified the interpretation of any particular isotherm, since the various shapes of these are related to the adsorption mechanisms involved.

The significance of X-ray data in confirming the interpretation of adsorption isotherms is shown for instance in relation to the adsorption of aromatic compounds. These frequently give rise to S-type isotherms, and Giles *et al* (1960) ascribe the inflection on these isotherms to reorientation of the aromatic molecules at the surface. A study of pyridine adsorption by montmorillonite (Greene-Kelly, 1955b) gave S-type isotherms and an increase in the interlamellar separation corresponding to the isotherm inflection was observed. Giles *et al* (1960) state that linear adsorption isotherms are associated with an increased availability of sites as adsorption proceeds. Greenland, Laby and Quirk (1962) observed this type of adsorption isotherm for glycine and its peptides on calcium montmorillonite, and X-ray studies showed that the basal spacing increased as adsorption proceeded, so making an increased number of sites available.

The systems which have been most extensively studied by determination of adsorption isotherms and X-ray methods are those involving montmorillonite and various amino compounds. Much of this material has recently been reviewed by Weiss (1963). Amines are readily adsorbed in the cationic form by exchange for inorganic ions. The adsorption isotherms obtained are characteristically Langmuir or L-type (Giles *et al* 1960) corresponding to

n in which a fixed number of sites participates. The initial slopes of the isotherms increase as the number of carbon atoms in the amino compounds increase (Jordan, 1949; Sieskind and Wey, 1958; Cowan and White, 1958; Weiss and Michel, 1958a; Greenland and Quirk, 1960; McAtee and Hackman, 1964; Theng 1964), showing that the bonding strength is greater with the larger cations. The non-standard free energies of adsorption derived from the exchange equilibria show that the increment per CH_2 group is approximately 400 cals per mole, the same value as found for the adsorption of n-alkyl compounds at liquid-liquid and gas-liquid interfaces. This is the energy due to the van der Waals forces between CH_2 groups (Davies and Rideal, 1961). If the number of carbon atoms does not exceed 8, adsorption does not proceed beyond the cation-exchange capacity of the clay, but for larger cations it is limited only by the surface area of the clay. With these cations van der Waals interactions dominate the adsorption process so that the isotherms become H-type rather than L-type, and the alkyl chains project in a plane at right angles to the surface. The principal van der Waals interactions are between the absorbed molecules rather than between the adsorbed molecules and the clay surface.

Amino acids are adsorbed in the cationic form (Talibudeen, 1955; McLaren, Peterson and Barshad, 1958; Sieskind and Wey, 1959; Sieskind, 1960a,b; Greenland, Laby and Quirk, 1962, 1965a), and also as dipolar ions (Greenland, Laby and Quirk, 1962, 1965b). Adsorption as the cation takes place only below the isoelectric pH of the amino acids and is greater for the more basic ones (Talibudeen, 1955; Sieskind and Wey, 1959). However physical adsorption forces also contribute to the adsorption process. These are composed of an interaction between the dipoles of the amino acids and the exchangeable cation and charged surface sites on the clay, and of dispersion forces between the surface and the amino acid molecules (Greenland, Laby and Quirk, 1965a). The significance of physical adsorption forces in the adsorption is shown by the fact that they are also adsorbed, without proton transfer or cation exchange, by sodium and calcium montmorillonite at or near the isoelectric pH of the amino acids (Greenland, Laby and Quirk, 1965b).

The hypothesis that proteins constitute a considerable proportion of soil organic matter has stimulated a number of studies of protein adsorption by montmorillonite. Results obtained by Ensminger and Gieseking (1942) indicated that adsorption by clays would reduce the rate at which proteins were decomposed by microorganisms. X-ray examination of the adsorption complexes showed that adsorption occurred on interlamellar surfaces where presumably the protein was inaccessible to microorganisms. Other studies (Gieseking, 1939; Hendricks, 1941; Ensminger and Gieseking, 1941; Weiss and Hofmann, 1951; Talibudeen, 1955; Armstrong and Chesters, 1964) have shown that both cation-exchange and physical adsorption forces contribute to the adsorption process. This accords well with the results obtained with amino acids. Pinck, Dyal and Allison (1954), Talibudeen (1955), McLaren, Peterson and Barshad (1958) and Armstrong and Chesters (1964) have shown that globular proteins when adsorbed may uncoil, and give rise to interlamellar spacings of 5-10A, or may not uncoil, or only partly do so, when interlamellar spacings of 30A and more are observed. The number of proteins whose adsorption has been studied is insufficient to enable firm conclusions to be reached about the significance of the change in configuration, but analogy with their behaviour at other surfaces (Cumper and Alexander, 1950, 1951; Davies, 1953; Tanford, 1961; Davies and Rideal, 1961) suggests it will be very important.

The amounts of protein adsorbed are large (up to 2.4 g/g of montmorillonite) and limited by the amount of surface, and not the number of charged sites on the surface (McLaren *et al*, 1958; Armstrong and Chesters, 1964). Maximum adsorption was observed at or near the isoelectric pH of the protein. Armstrong and Chesters (1964) suggested that the decrease in adsorption in more acid conditions was due to increased competition with hydrogen ions, but as adsorption of amino acids continues to increase as the pH decreases (Sieskind and Wey, 1958b) this seems unlikely. A more probable explanation is that as the solubility of the protein is least near the isoelectric pH, it is more readily removed from solution than at other pH's.

The adsorption of a number of cationic organic polymers by montmorillonite has also been studied (Ruehrwein and Ward, 1952). The same general principles appear to apply.

As might be expected, negatively charged compounds are not readily adsorbed on the negatively charged surfaces of montmorillonite. However, significant adsorption can occur through a polyvalent exchangeable cation. Meyer (1935) suggested Ca^{++} ions acted as bridges between clay and organic anions, and this has been supported by Peterson (1948). Van Olphen (1950) suggested a similar mechanism to account for the adsorption of tannates and some other anions. Weiss (1959) considers that such bridge linkages provide a general mechanism for anion adsorption by clays. Greenland (1956b) observed that gluconic and glucuronic acids were adsorbed at high pH, when excess Ca^{++} ions were present. It is also possible that chelation occurs between organic compounds such as EDTA and exchangeable cations which form stable chelates at neutral pH (cf. Wallace and Lunt, 1956; Bodenheimer *et al*, 1962).

Some criticisms of the concept of formation of bridge linkages by polyvalent cations have appeared (Wild, 1953; Bach and Deuel, 1953). However, the neutralization of charges, which are separated by distances of the order of 10A and more, by a single multivalent cation is unlikely. The data of Edwards, Posner and Quirk (1965) indicate that the charges cannot be considered to be distributed as a more or less uniform negative field. Fripiat and his collaborators have recently presented detailed evidence from infra-red, conductivity and other studies that in fact the water in calcium montmorillonite is more dissociated than ordinary water (Calvet *et al*, 1965).

Thus some hydroxyl and hydroxonium ions should be present on the clay surfaces so that the formation of a "bridge" linkage to another anion could occur simply by displacement of an hydroxyl ion.

Only small amounts of some non-polymeric organic anions have been reported to be adsorbed by sodium montmorillonite (Goring and Bartholomew, 1950, 1952; Frissel, 1961; Arlidge and Anderson, 1963) and as Frissel has shown, the repulsion of the anion is the dominant process and a negative adsorption is generally recorded. The small amounts of positively adsorbed material may well be associated with the presence of traces of aluminium or aluminium oxides on the surface of the clay. The amount of adsorption is higher when the pH falls below 6. This has been ascribed to the development of positive charges at the edges of the clay lattice. However, for montmorillonite it has recently been shown that such charges are extremely small or zero (de Haan and Bolt, 1963; Edwards, 1964). It seems more likely that the adsorption is again due to association with adventitious aluminium oxides, the charge on which also increases as the pH decreases (Deshpande, Greenland and Quirk, 1964), and which are invariably formed from montmorillonite in acid conditions. The positively charged oxide or hydroxide may of course form a bridge between the anion and the clay surface.

The adsorption of organic polyanions has received considerable attention because of the use of these materials as soil conditioners. Ruehrwein and Ward (1952) showed that although solutions of sodium polymethacrylate added to clay suspensions strongly influenced their physical properties it was not adsorbed in the interlamellar regions. Hagin and Bodman (1954), Emerson (1956b), Holmes and Toth (1957) and Ahlrichs (1962) obtained similar results for other polyanions. Emerson (1955) suggested that the complexes formed be termed "peripheral" as the polymer is attached only to the edges of the clay lattice. Lynch *et al* (1957) found small amounts of alginates and pectates adsorbed by Na and H montmorillonite (they report larger amounts adsorbed by the calcium clay, but this may have been due to precipitation of the calcium alginates and pectates, rather than adsorption). Where bonding occurs predominantly at external surfaces, montmorillonite offers no advantage in adsorption over other clays, since it is apparently less likely to develop positive charges at the edges than kaolinite. The adsorption of anionic materials has therefore been studied in more detail with kaolinite. This will be discussed below.

Very few studies of the adsorption of uncharged organic compounds from aqueous solution by montmorillonite have been reported. Greenland (1956a,b) showed that sugars were adsorbed, but only in very small amount unless the concentration was very high. Oligosaccharides were more strongly adsorbed than monosaccharides, and methylated sugars more strongly than the non-methylated. This latter effect is probably due to the very strong hydration of the hydroxyl groups of the non-methylated sugars that tends to prevent their adsorption. Brindley and Hoffmann (1961) found that ethylene glycol was not adsorbed in measurable amount from aqueous solution. Of the alcohols, ethers and ketones studied (Hoffmann and Brindley, 1960) only those with more than six carbon atoms in the molecule were readily adsorbed from solution.

Uncharged polymers are adsorbed in large amount and strongly retained (Lynch, Wright and Cotnoir, 1956; Emerson, 1955; Ruehrwein, 1957; Brindley and Rustom, 1958; Greenland, 1963; Emerson and Raupach, 1964). The exchangeable cation influences the amount of adsorption very markedly, because of its influence on the dispersion of the clay, and the accessibility of interlamellar surfaces. Most of the work reported has been with hydroxylic compounds, and it has generally been suggested that the compounds are hydrogen-bonded to the clay surface. No satisfactory evidence to establish this has been presented, and the fact that polyethylene glycols, which are ethers and contain only end-group hydroxyls are quite strongly adsorbed (Greenland, unpublished) suggests that multiple dispersion forces associated with the many surface segment contacts per molecule, and the entropy factor, may be the most important contributors to the adsorption of these large molecules.

Most of the studies of adsorption of uncharged polymers have shown that once adsorbed it is extremely difficult to desorb the polymer molecules (Silberberg, 1962b; Emerson, 1963; Greenland, 1963). This is to be expected when adsorption is due to a large number of weak bonding points, since although any one segment of the polymer may be readily desorbed, it is highly improbable that all segments will be desorbed simultaneously, the condition necessary if the polymer is to be separated from the clay particle. The detailed theoretical treatment of Silberberg (1962a,b) has shown that the strong adsorption by multiple weak surface-segment interactions can be accounted for very satisfactorily, and that theory also predicts irreversibility and collapse of the polymer to the surface, provided the polymer molecule is sufficiently flexible.

(iii) Spectrophotometric studies.

When specific groups of an organic molecule interact with a surface on which the molecule is adsorbed, the movements of the atoms composing those groups will be modified. This will result in a change in the frequency at which infra-red radiation is absorbed. Consequently such changes are potentially useful in the study of adsorption mechanisms (cf. the reviews by Eischens and Pliskin, 1958, and Sheppard, 1959). It is necessary that the absorbent has a large surface area so that sufficient organic material is adsorbed to provide a measureable spectrum and that the adsorbent should not obscure spectral changes due to the adsorbed compound. Soil colloids have the necessary surface area, and although the spectra of clay minerals contain fairly intense absorption bands around 3µ and 8-12µ, elsewhere they are very clear. Thus except for hydroxyl absorption in the 3µ region organic molecules on montmorillonite can be effectively studied by infra-red techniques.

Tensmeyer, Hoffmann and Brindley (1960) compared the spectra of crystalline 2:5 hexanedione and 2:5:8 nonanetrione and of their complexes with montmorillonite supported in KCl discs with those of their solutions in carbon tetrachloride. The spectra of the crystals and clay-adsorbed material were very similar and both showed higher asymmetric deformation frequencies for the methylene groups of nonanetrione than did the solution in carbon tetrachloride. This they ascribed to weak C-H . . . O interactions "of a hydrogen-bonding type" in the adsorbed phase. However as Laby (1962) and Brindley and Hoffmann (1962) have subsequently pointed out no lowering of the C-H stretching frequencies which would be expected if C-H . . . O bonding occurred, was observed. The change in the deformation frequency might well be due to interactions within the electric field of the crystal or adsorbed layer other than C-H . . . O bonding. Laby (1962) examined the infra-red spectra of the montmorillonite complexes of methyl alcohol, p-dioxane and ethylene glycol between 3,800 and 2,700 cm^{-1}, using a spectrometer capable of detecting a change of 1 cm^{-1}, but no decrease in the C-H stretching frequencies was observed. Fripiat, Servais, and Leonard (1962) noted a change for diamines adsorbed on montmorillonite, but state that the nature of the interactions causing it are unknown. Thus until more convincing evidence is presented no importance can be attributed to C-H . . . O interactions in the formation of the complexes.

Shifts in the carbonyl-group stretching frequency of adsorbed compounds and the increase in intensity of the bonded O-H band at 3μ have been interpreted as due to the formation of hydrogen bonds with Si-OH groups at the edges of the montmorillonite lattice (French *et al* 1954; Kohl and Taylor, 1961; Larson and Sherman, 1964). However, Tensmeyer, Hoffmann and Brindley (1960) found similar shifts for interlamellar complexes of montmorillonite with ketones, and ascribed these to the effects of enhanced interactions between the adsorbed molecules. Tahoun and Mortland (private communication) observed similar shifts in the carbonyl frequency of urea and other amides adsorbed by montmorillonite, and have been able to establish that this is due to the association of the carbonyl group with the exchangeable cation. There is thus no unequivocal evidence for hydrogen bonding between surface and carbonyl groups. Fripiat, Servais and Leonard (1962) have shown that the N-H frequencies of adsorbed amines are shifted in a way indicative of hydrogen bonding, but again it was not possible to decide whether this was due to interactions between the adsorbed molecules themselves or between the adsorbed molecules and the surface.

Very few studies using visible or UV spectra have been published, although these might well provide useful information relating to the adsorption of aromatic compounds. For instance Bergmann and O'Konski (1963) were able to show that adsorption of methylene blue by sodium montmorillonite was associated with dye-dye interactions on the surface. There are greater practical difficulties associated with such studies than with work on the infra-red region.

Adsorption by other clay minerals and oxides

(i) Other clays with mica-type lattices.

The work of Weiss and his colleagues (Weiss, Mehler and Hoffmann, 1956a, b; Weiss, 1958b; Weiss, Michel and Weiss, 1959; Weiss, 1963) has shown that not only montmorillonite but vermiculite, illites and the micas themselves react with long chain alkyl ammonium compounds, to form interlamellar complexes. The reaction is however slower than with montmorillonite, e.g. it may require several months at 60°C for complete interlamellar expansion of a mica to occur. Differences between the minerals with mica-type lattices are due to differences in surface density of charge. Thus there are only small differences in the reactions of vermiculite and montmorillonite with organic compounds (cf. the data relating to vermiculite given by Walker (1958), and the results obtained by Greenland, Laby and Quirk (1965a, b) for the adsorption energies of amino acids on illite and montmorillonite). Although the strength of adsorption may be greater on more densely charged surfaces, the amount of adsorption is less because of the much lower surface area.

(ii) Kaolinites.

Kaolinites have important structural differences to the mica-type layer-lattice silicates; one basal face of the crystal is a silicate sheet but the other is a gibbsite sheet. Unlike the silicate sheet the gibbsite surface may not carry a charge (Weiss, 1959, 1963). The edges of the kaolinite lattice become positively charged at low pH (Schofield and Samson, 1954), and this charge may persist to relatively high pH's (Quirk, 1960). The positive charges at the edges enable it to form peripheral complexes with anionic compounds (Goring and Bartholomew, 1952; Michaels, 1954; Michaels and Morelos, 1955; Martin and Aldrich, 1955; Emerson, 1955; Mortensen, 1957). Although the pH at which most adsorption occurs is where the kaolinite is positively charged, Michaels and Morelos (1955) consider that the pH effect is due to its influence on polymer configuration, and that physical adsorption rather than ionic bonding is the most important adsorption mechanism.

Mortensen (1959) and Ahlrichs (1962) have shown that the adsorption of anionic polymers is greater in the presence of salts, or of cations which decrease the zeta potential of the polymer and the clay. Electrostatic repulsion between clay and polymer is reduced so that a closer approach is possible, and physical interactions can become important, although the interaction presumably involves relatively few, uncharged segments of the polymer. Mortensen (1959) considered that as well as reducing the zeta potential, the presence of polyvalent cations enhanced anion adsorption on kaolinite by formation of "bridge" linkages; coordination complexes with such ions on the clay surface might also be formed.

Alkylamines are also adsorbed by kaolinite (Weiss, 1959; Greenland and Quirk, 1962, 1964) although

adsorption may be restricted for some kaolinites to the silicate basal surface (Weiss, 1959). Brindley, Bender and Ray (1963) by determination of a few isolated points of the adsorption isotherm have shown that a kaolinite can adsorb acetoacetic ethyl ester and oxydipropionitrile in amounts more than sufficient to form a complete surface monolayer.

Although it has been known for some time that organic compounds can replace the interlamellar water layer in hydrated halloysite (MacEwan, 1946, 1948; Caillère *et al* 1950) and it has recently been established that many kaolinites show interlamellar expansion when treated with ammonium or potassium acetate (Wada, 1961) urea (Weiss, 1961a) and hydrazine (Weiss *et al*, 1963), it seems unlikely that these internal surfaces are significant in the adsorption of organic compounds in soils.

(iii) Oxides and allophane.

Many studies of adsorption of organic compounds from aqueous solution by silica and alumina have been reported (cf. the data quoted by Giles *et al*, 1960). The surface properties and surface areas of these materials vary considerably, depending on their origin and past history, and this causes very important differences in their behaviour as adsorbents. Very little is known of the surface properties of the oxide materials in soils. Thus there is little value in reviewing in detail the rather diverse literature on adsorption by oxides, since its relevance to adsorption in soils cannot be assessed. It has been known for some time that the oxides in soils, unlike the clay minerals, may be predominantly positive (van Schuylenborgh and Sanger, 1949; Schofield, 1949; Schuylenborgh, 1950) and recent work has confirmed this (Sumner, 1962, 1963) although it now seems possible that the positive charge is due only to aluminium oxides, iron oxides, unless freshly precipitated, being negatively charged in the pH range of many soils (Deshpande, Greenland and Quirk, 1964). Allophane in soils may also carry a considerable positive charge.

It is to be expected that the positively charged oxides will be more active than other soil materials in the adsorption of organic anions, but there is no work with simple organic anions and soil oxides to establish this. There is however much relevant data obtained using humic and fulvic acids, and this will be discussed in part II of this review.

4. Conclusions from Studies with Clay Minerals and Oxides and Organic Compounds of known Chemical Structure

Several important generalisations emerge from studies with defined materials. Organic compounds with molecular weights of about 150 and less are not adsorbed at all, or only very weakly adsorbed, from aqueous solution, unless they carry a charge and can enter ion-exchange reactions. Larger molecules, whether charged or not, may compete effectively with water molecules for the surfaces and uncharged polymers such as polyvinyl alcohol can be very strongly adsorbed. Spectroscopic studies indicate that specific interactions with the surface, such as the formation of a hydrogen bond, do not necessarily contribute to the adsorption energy, but concentration of the species on the surface can enable interactions between the molecules to become important and enhance the adsorption energy. The failure to obtain evidence of specific interactions between organic compounds and the surfaces and the increase in adsorption energy with increasing size of the adsorbed molecules, indicate the importance of non-specific van der Waals (dispersion) forces in the adsorption process. Such dispersion forces are additive for each point of contact between the adsorbed molecules and the surface. If the adsorbed molecule displaces water molecules from the surface, it is also probable that the entropy factor will favour the adsorption process. For a polymer molecule to be strongly adsorbed it would seem to be necessary either that the molecule be ionically bound to the surface, or that it be large and planar or sufficiently flexible to make a large number of points of contact with the surface.

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Table 1. Proportion of soil organic carbon contained in the clay-organic complex.

Authors	*Soils*	*Method of Separation*	*Total C in soil %*	*C in clay-organic complex as % of total soil C*
Hénin & Turc, 1950	Rendzina	Sedimentation in benzene-bromoform, s.g. 1.75	—	66.5
Khan, 1959	Podzol	Sedimentation in Toulet solution, s.g. 1.8	1.6	89.6
	Chernozem		4.4	85.2
Monnier *et al*, 1962	Silt under old pasture	Sedimentation in ethanol-bromoform, s.g. 2.0	2.34	77.5
Roulet *et al*, 1963	Rendzina	"Flotation sieving"	5.8	54.3
	Brown earth		3.2	68.1
Greenland & Ford, 1964	Red-brown earth	Ultrasonic dispersion and sedimentation in bromoform-pet. spirit, s.g. 2.0	2.23	71.5
	Rendzina		5.8	68.4
	Lateritic red earth		1.7	97.8
	Solodized solonetz		1.04	76.4
	Solonized brown soil		0.58	51.6

Table 2. Forces involved in the interaction between clays and organic compounds.

1. Coulombic attractions between	Negatively charged surface and positively charged organic compound Positively charged surface, or ion or oligo-ion* at surface, and organic anion		
2. Van der Waals forces, composed of			
(a) Polar: Charge-dipole interactions Dipole-dipole interactions (including H-bonding) Charge-induced dipole interactions Dipole-induced dipole interactions (b) Non-polar: Dispersion forces		between	surface and organic compound adsorbed molecules of similar species adsorbed molecules of dissimilar species

* e.g. positively charged hydroxy aluminium oligomers.

Table 3. Summary of properties of components of the systems which influence the adsorption of organic compounds by clays.

Properties of surface	*Properties of organic compound*	*Properties of medium*
Extent (total surface area)	Charge Size	Those which affect its behaviour
Accessibility (size and tortuosity of pores)	Polarity Polarisability	(1) as solvent for organic compound
Chemical nature of atoms forming surface (O or OH)	Shape Flexibility	(2) as competitor with organic compound for sites on clay surface
Charges at surface (spatial density and distribution, origin)		
Exchangeable ions on surface		
Configuration of surface		